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EFFECT OF STRESS ON BOUNDARY LUBRICATION BY ADSORPTION

David V. Burke

EFFECT OF STRESS ON BOUNDARY LUBRICATION
BY ADSORPTION

by

DAVID V. BURKE, JR.

B. S., UNITED STATES NAVAL ACADEMY

(1961)

SUBMITTED IN PARTIAL FULFILLMENT
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DEGREES OF NAVAL ENGINEER
AND MASTER OF SCIENCE IN
MECHANICAL ENGINEERING

at the

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY

June 1970

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EFFECT OF STRESS ON BOUNDARY LUBRICATION BY ADSORPTION

By

DAVID V. BURKE, JR.

Submitted to the Department of Naval Architecture and Marine Engineering and the Department of Mechanical Engineering on June 4, 1970 in partial fulfillment of the requirements for the degrees of Naval Engineer and Master of Science in Mechanical Engineering.

ABSTRACT

This thesis investigates the effect of stress on the physical adsorption of methanol. It is found that methanol, adsorbed from an atmosphere of nitrogen saturated with methanol vapor, effectively lubricates copper when contacting a thick layer of tin. Methanol does not, however, lubricate when the copper contacts a thin layer of tin. The contact with the thin layer of tin has a higher stress level as the harder substrate supports the load. Thus the critical stress, defined as the stress at which the lubricant desorbs, is greater than 6 kg/mm^2 (the penetration hardness of tin). Effectiveness of lubrication is qualitatively measured by visual observation of transfer of tin to the copper, as significant changes in contact resistance were not found.

Elastic contact for tungsten specimens showed a critical stress of less than 17.4 kg/mm^2 based on visual indications of surface damage at this stress level. Contact resistance data is reported but is erratic and thus inconclusive.

Thesis Supervisor: Brandon G. Rightmire
Title: Professor of Mechanical Engineering

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I wish to express my appreciation first of all to the United States Navy for sponsoring this program of graduate study as part of my career program as well as for financial support in preparing this thesis.

Professor Brandon G. Rightmire provided not only the theoretical basis for this work but also advice and helpful suggestions for which I am most grateful.

The mechanics of the experiment and construction of the apparatus went much better with the help and advice of Mr. Sam Marcolongo and Mr. Jack Leach than the author could have accomplished on his own.

The forbearance, encouragement and ultimately the typing of my wife, Barbara, were indispensable in performing the work necessary for this investigation and for this support I am most appreciative.

Finally, the patience and understanding of Laurie, Dave and Chris are appreciated as they missed doing something because "Daddy's going to work in the laboratory again!"

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INTRODUCTION

Boundary lubrication is defined as a "condition of lubrication in which the friction between two surfaces in relative motion is determined by the properties of the surfaces and by the properties of the lubricant other than viscosity." [1]* In many cases, the lubrication provided may be considered poor as the coefficient of friction may be high i.e., approximately .1 to 1.0. However, the effectiveness of a boundary lubricant is better measured by metal pickup [2]. A good boundary lubricant may reduce friction by a factor of only 20 but metal transfer may simultaneously be reduced by a factor of 20,000 [6].

Thus, the high coefficient of friction and the fact that any metal-to-metal contact occurs at all, makes boundary lubrication seem to compare unfavorably to other forms of lubrication where a full film of lubricant is maintained, sufficient to completely separate even fairly rough surfaces, eliminating metal-to-metal contact and reducing friction by several orders of magnitude. However, a boundary lubricant may serve as the last barrier before seizure when relative motion ceases, such as in a stopped automobile engine or where other forms of lubrication are not possible or practical e.g., at elevated temperature.

---

*Numbers in brackets refer to references listed in the bibliography.

Adsorbed films from our normal environment serve to prevent seizure of even "clean" metals [3] and their removal is a challenge in the technology of cold welding and other joining processes [4].

Three mechanisms are generally proposed to explain boundary lubrication [1].

1. Physical adsorption or physisorption
2. Chemical adsorption or chemisorption
3. Chemical reaction

Physisorption is particularly marked by a low heat of adsorption (2,000 to 10,000 cal/mole) and reversibility. The adsorbed molecules retain their own electrons.

Chemisorption is distinguished by high heat of adsorption and is not completely reversible. The electrons of the adsorbent are shared with those of the surface but the surface atoms do not leave their lattice.

Unlike both of the mechanisms of adsorption, chemical reaction alters the composition of the surface. Improvement occurs when the compound formed in the film has lower shear strength than the base metal and when accelerated corrosion does not make up for the reduction in wear. The surface atoms can and do leave their lattice.

Physical adsorption is the mechanism under investigation in this study.

BACKGROUND

There is no scarcity of published information in the field. "Boundary Lubrication - An Appraisal of World Literature" [5] provides a comprehensive survey and contains abstracts of over 1,500 articles and books on the subject of boundary lubrication.

In the next few pages, a brief synopsis of a very few papers will be presented to set the stage for the purpose of this investigation.

SIR WILLIAM B. HARDY

Credit is generally given to Sir William B. Hardy as the pioneer in boundary lubrication [2]. In one of his later papers [6], he proposed a relation for the coefficient of friction that is dependent on the nature of the solids, the lubricant molecular structure (the coefficient of friction decreasing with molecule chain length) and temperature. There was no dependence on bulk lubricant properties.

In an extensive test program, investigating over 100 pure organic compounds, he observed stability (i.e. an equilibrium position between parallel test surfaces under load) to pressures of 10 kg/mm^2. He also noted no differences in properties when testing in liquid or in an atmosphere containing saturated vapor of the lubricant.

EFFECT OF TEMPERATURE - D. TABOR AND E. RABINOWICZ

In 1940, D. Tabor observed that "in cases where boundary lubrication occurs" satisfactory behavior at room temperature

does not necessarily imply good lubrication at elevated temperature [7]. He notes that the effect is reversible and attributes the phenomenon to desorption or disorientation of the lubricant film.

Eleven years later, two transition temperatures were identified [8]. A marked increase in metal transfer occurred at a temperature near the melting temperature of the film while further deterioration was noted at higher temperature. Even though the surface was visibly covered with lubricant, the friction and metallic transfer were similar to unlubricated conditions. At both temperatures, the effects were reversible. It was proposed that at the lower temperature, disorientation of the film occurred and desorption followed at the higher temperature.

THE EFFECT OF STRESS - D. TABOR AND S. C. COHEN

An apparent anomoly is observed while investigating lubrication of polymers [9]. It is found that water does not lubricate glass sliding on glass nor polythene sliding on polythene at very low sliding speeds. However, water does lubricate glass sliding on polythene. The explanation proposed is that a water film is weakly adsorbed onto the glass surface. Under the low contact stress with polythene, the film remains adsorbed but the much higher contact stress of glass on glass causes desorption of the film. The film on the glass is stable under stresses of 1 - 2 kg/mm^2 for a "protracted period." The possibility of hydrodynamic effects

is discounted because the effect could not be observed with other fluids.

THE EXPLANATION - B. G. RIGHTMIRE

In a paper presented at the American Society of Mechanical Engineers Winter Annual Meeting in November 1969, B. G. Rightmire develops the theory for stability of a mono-layer of physisorbed molecules and explains the effects of stress and temperature [10].

It is shown that a meta-stable state can exist with almost the entire opposing surfaces separated by a physically adsorbed mono-layer of molecules. The layer is stable until either a "critical stress" or a "critical temperature" is exceeded in which cases the molecules desorb and a more stable state, that of metal-to-metal contact, results.

THE SPECIFIC PROBLEM UNDER INVESTIGATION AND SUMMARIZED PROCEDURE

This study undertook to investigate the effect of stress at room temperature on boundary lubrication by physisorption. It was desired that a relatively simple organic molecule serve as the "lubricant" so that it could be eventually compared to the theory [10]. Methanol was chosen.

The effects of stress were to be studied by noting changes in electrical resistance between two surfaces contacting with a known stress distribution, exposed to an inert gas (Prepurified Nitrogen) saturated with the methanol vapor.

Observations were also to be made of the specimens to check for effects of metal-to-metal contact, mainly surface damage or material transfer.

Relative motion must be imposed in order to supply the activation energy which is required to enable the adsorbed molecules to reach equilibrium and thus damage to the surface is to be expected unless the surfaces are completely separated by a physisorbed film.

RESULTS AND CONCLUSIONS

The results of this investigation will be presented in two sections categorized by the type of specimens used as follows:

A. tungsten versus tungsten

B. copper versus tin

The results of the copper and tin investigation are further divided into three sections defined in the introduction to each section.

A. TUNGSTEN VERSUS TUNGSTEN

Contact resistance measurements and visual observations were taken after contact and relative motion between two electropolished tungsten wires prepared as described in Appendix C. When visual observations were made, the expected area of contact was examined before and after the imposed motion and resistance measurements.

A summary of the significant measurements and observations is presented in Table 1. A more detailed summary of results is presented in Appendix D.

TABLE 1

SUMMARY OF RESULTS ON TUNGSTEN VERSUS TUNGSTEN

Atmosphere	Nitrogen saturated with methanol	Nitrogen only
Load	1/6 to 12 grams	1/3 to 1 gram
$\sigma (kg/mm^2)$	17.4 to 72.2	22.0 to 31.6
σ / J	$.455 \times 10^{-3}$ to 2.04×10^{-3}	$.615 \times 10^{-3}$ to $.89 \times 10^{-3}$
Resistance	Generally an ohm or less at 2/3 gram to 0.05 ohms at 12 grams. At 1/3 gram, values from .37 to 5,000 ohms were measured, but it was impossible to reproduce consistent measurements	Generally high and very erratic. Estimated average values from about 10 ohms to about 400 ohms were obtained. Lower resistance was not necessarily found at the higher loads.
Visual appearance	Even at 1/6 gram, surface disturbance was evident. The surface appeared discolored (light brown) and appeared to have small pits in the apparent contact area. At the higher loads larger, pit-like areas were visible.	Surfaces appeared scratched in the apparent contact area.

Note 1. σ = maximum apparent hertzian stress calculated for an elastic contact between cylinders

$J = E/(1-\nu^2)$

E = Young's modulus

ν = Poisson's ratio

The conclusions based on these measurements and observations are as follows:

1. An atmosphere saturated with methanol vapor reduces wear or changes the characteristics of wear, even at high stress levels (72.2 kg/mm^2). The high and erratic resistance measurements in nitrogen are thought to be due to debris from the increased wear.

2. Complete lubrication, i.e., complete separation of the tungsten surfaces, is not accomplished even at lowest attainable stress levels (17.4 kg/mm^2). This is indicated by the evidence of surface damage and the lack of consistently high resistance measurements. Therefore, the critical maximum apparent stress is less than 17.4 kg/mm^2 ($\sigma/J = .455 \times 10^{-3}$).

B. COPPER VERSUS TIN

1. Electropolished Tough-Pitch Copper on Copper Coated with a "Thick" Layer of Tin

The copper specimen was a .050 inch diameter wire electropolished using the polishing procedure for copper described in Appendix C. This was ordinary tough-pitch copper wire and even after polishing many pits or elongated holes were obviously visible when observed visually, magnified 300 times.

The tin specimen was prepared by melting a globule of ACS reagent grade tin and allowing it to solidify on a .050 inch copper wire. The approximate thickness was about

.040 inches measured with a micrometer. The surface was cleaned with methanol to remove flux, cut with a razor blade to expose fresh metal and then rolled with a glass rod to smooth the surface.

The results of the tests with these specimens are shown in Table 2 and Figures 1 and 2. These data were obtained following motion at one hertz for one minute between the specimens under the load specified.

TABLE 2

RESULTS OF ELECTROPOLISHED TOUGH-PITCH COPPER WIRE VERSUS A THICK COATING OF TIN

Atmosphere	Resistance (ohms) after motion	Visual appearance of apparent contact area after motion
At a load of 1/6 gram:		
Air (no special atmosphere supplied)	3,750	blackened area
Methanol saturated nitrogen	2.17×10^{-3}	area barely visible difficult to evaluate
"	4.03×10^{-3}	slight discoloration
Nitrogen only	23.3×10^{-3}	brownish area with scratches
"	16.6×10^{-3}	area with dark pit-like spots
At a load of 5 grams:		
Nitrogen only	1.56×10^{-3}	large pitted like area with darkened spots and light shiny scratches (see Figure 1)
Methanol saturated nitrogen	1.25×10^{-3}	generally clear area with a shiny film (see Figure 2)
Nitrogen	10×10^{-3}	scratch marks with material that appears to be tin
Methanol saturated nitrogen	1.87×10^{-3}	smooth shiny area, same color as tin

Notes 1. Stress level assumed to be 6 kg/mm^2, i.e. plastic contact at hardness of tin, $\sigma/J = 1.26 \times 10^{-3}$

2. A new contact zone was used each time.

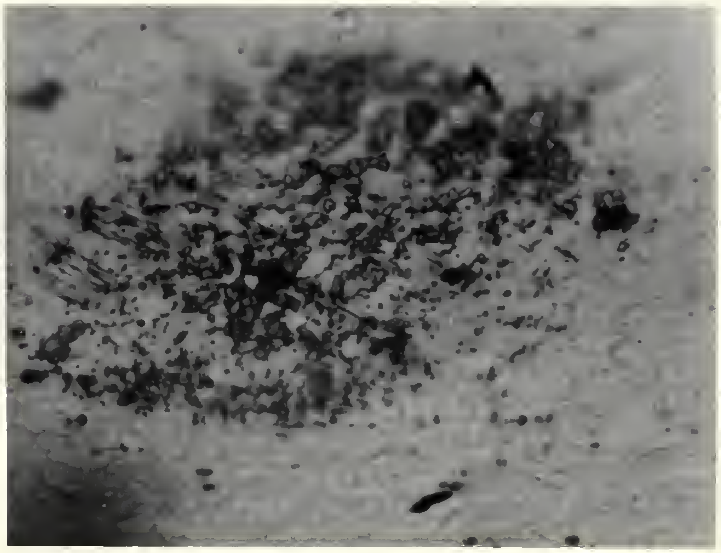

FIGURE 1

Ordinary electropolished copper specimen after contact with thick tin coated specimen and imposed motion under 5 gram load in atmosphere of nitrogen (300X). Some scratches with tin-like material were observed but are not evident in the picture.

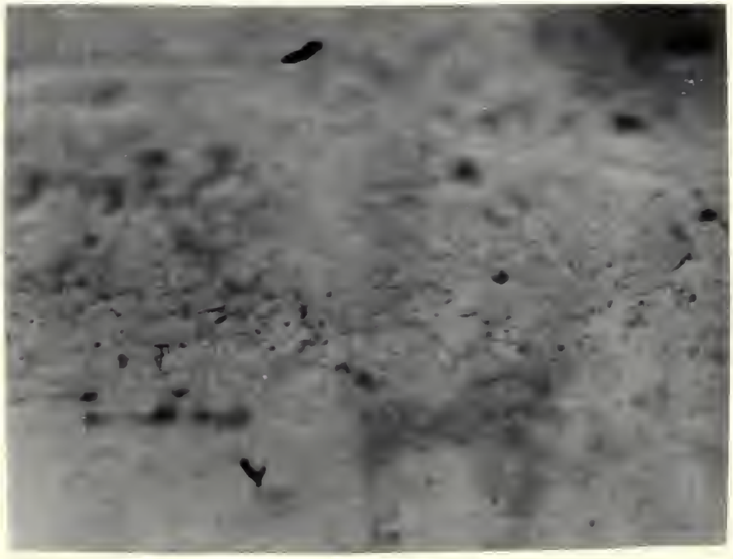

FIGURE 2

Ordinary electropolished copper specimen after contact with thick tin coated specimen and imposed relative motion under 5 gram load in methanol saturated nitrogen (300X). A film of tin-like material appears on the surface.

The conclusions drawn from these observations is that methanol has an effect in getting smooth transfer resulting in both a lower resistance and film of tin on the copper. However, material transfer is not eliminated.

2. Electropolished Oxygen-Free High-Conductivity (OFHC) Copper Versus "Thick" Tin

The copper specimen for this test was a .200 inch rod of OFHC copper. The rod was electropolished as described in Appendix C. The tin specimen was the same specimen described above in Section B1.

Measurement of resistance and optical examination of the copper rod after motion at one hertz for one minute resulted in the following typical results at a load of 5 grams.

Atmosphere	Resistance (ohms)	Observation
Nitrogen	16×10^{-3}	large darkened area, many black spots (see Figures 3 and 4)
Methanol saturated nitrogen	1.59×10^{-3}	small pit-like spots at edge of area, film may be present but if so it appears extremely thin (see Figures 3 and 5)

It appears from these results that methanol vapor is effective in lubricating under these conditions. Transfer of tin appears virtually eliminated. As before, plastic contact with the tin is assumed and thus the stress is 6 kg/mm^2.

This stress level, equivalent to the recorded indentation hardness of tin [2], may be low by a factor of 2 in light of recent research [12]. Williamson and Hunt have measured the actual contact area under conditions similar to the hardness test and find the area to be one-half of the indenter and propose an actual stress level equal to twice the standard recorded hardness.

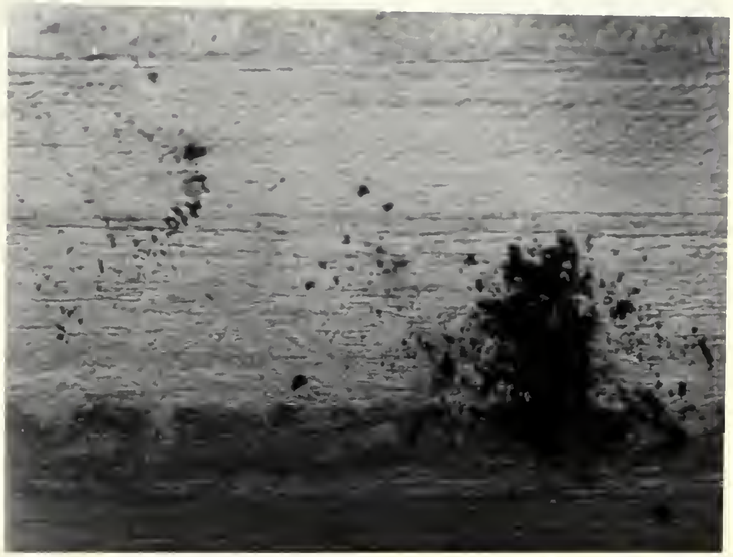

FIGURE 3

Electropolished OFHC copper specimen showing two contact areas at 5 gram load after motion at 1 hz for one minute against thick tin coated specimen.

Zone on left at center followed contact and motion in atmosphere of nitrogen saturated with methanol.

Area at lower right followed contact and motion in atmosphere of nitrogen only (150X).

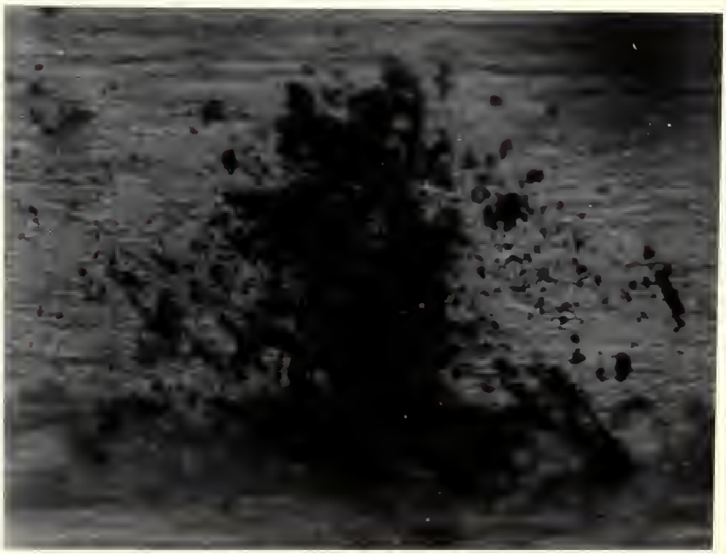

FIGURE 4

Enlargement of contact zone with nitrogen atmosphere (300X).

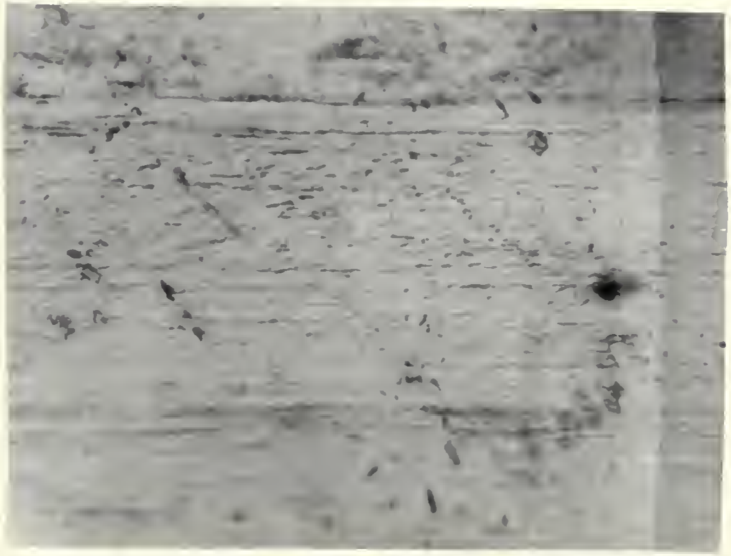

FIGURE 5

Enlargement of contact zone with methanol saturated nitrogen (300X). A thin film of tin-like material appears to cover about three-quarters of the contact zone.

3. Electropolished OFHC Copper Versus Copper with a "Thin" Coating of Tin

The copper specimen was the specimen described above in Section B2. To prepare the "thin" coating, the electropolished .050 inch copper wire previously used as the copper specimen in obtaining the results of Section B1 was coated with the thinnest coating of tin that the inexperienced author could accomplish. The thickness was not measurable with a micrometer but an estimate of .0003 inches was calculated based on a weight change of .0043 grams in the copper specimen after tinning and cleaning and an estimate of the fraction of the circumference and measurement of the length covered.

Typical results with these specimens are as follows for a load of 5 grams.

Atmosphere	Resistance (ohms)	Visual Observation
Nitrogen	1.5×10^{-3}	Smooth, grooved surface of tin-like material on copper specimen. The tin coating did not appear to be completely penetrated.
Methanol saturated nitrogen	1.5×10^{-3}	Same as above with nitrogen (see Figure 6)

Assuming that the film is thin enough so that the copper substrate supports the load and the tin shears at the surface the maximum apparent hertzian stress for elastic

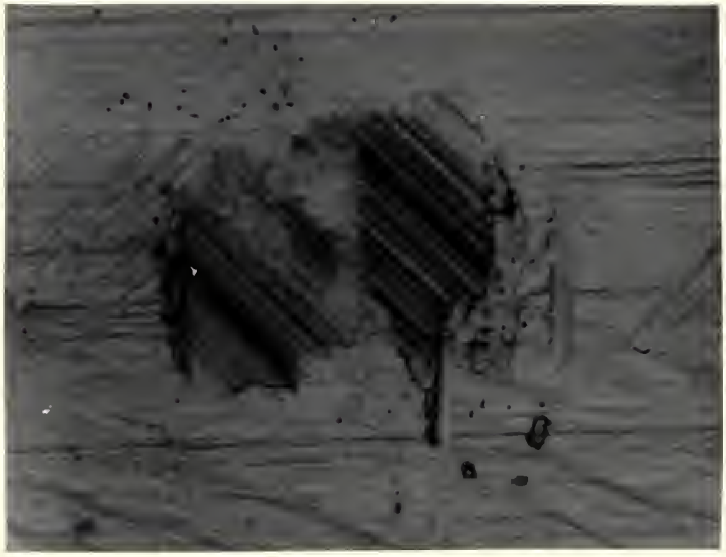

FIGURE 6

Electropolished OFHC copper specimen after contact with thin tin coated specimen under a load of 5 grams and after motion at 1 hz for 1 minute. The darkened areas, compared to the background, appeared lighter and like tin in color when examined visually even though they appear darker in the photograph (400X).

contact is 31.8 kg/mm^2 and $\sigma/J = 2.36 \times 10^{-3}$. If the copper is assumed to plastically support the load the stress would be 80 kg/mm^2 [18].

Thus since the materials, load and atmosphere are the same as in Section B2 above, only the stress has changed and this in turn has greatly increased the transfer of tin to the copper.

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Thus [illegible]

the same as [illegible]

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TABLE 3

SUMMARY OF RESULTS

Specimens	Stress (kg/mm^2)	σ/J	
Tungsten on tungsten	17.4 to 72.2	$.455 \times 10^{-3}$ to 2.04×10^{-3}	Incomplete monolayer. High resistances however at low loads. Some lubrication at highest loads. Critical stress less than 17.4 kg/mm^2.
Smooth OFHC copper on thick tin coating	6.0	1.26×10^{-3}	Essentially no transfer of tin
Smooth OFHC copper on thin tin coating	31.8 elastic 80.0 plastic	2.36×10^{-3} 5.94×10^{-3}	Smooth transfer of tin to copper. Critical stress greater than 6 kg/mm^2 but less than 80 kg/mm^2.

DISCUSSION OF RESULTS AND RECOMMENDATIONS

The conclusion that stress does affect the effectiveness of lubrication by methanol, when present as a saturated vapor at room temperature, as predicted by Reference 10, is based on the essential prevention of transfer of tin to the smooth copper surface from the thick tin coating whereas transfer occurs when the coating is thin. Since all the parameters controlled by the investigation, i.e. speed and time of imposed relative motion, atmosphere, load and material remained the same while only the thickness of the tin layer was altered, it is concluded that only the stress has changed. This conclusion is supported for example in Reference 2 and Reference 11 and this principle forms the basis for solid lubrication [16]. It must be assumed, however, that the layer is thin enough for the substrate to assume the load, and since transfer occurred, as it had not with a thick layer previously, this assumption is felt to be justified.

Thus the critical stress is greater than 6 kg/mm^2 ($\sigma/J = 1.26 \times 10^{-3}$) and less than 31.8 kg/mm^2 ($\sigma/J = 2.36 \times 10^{-3}$), assuming the substrate deforms elastically. A stress equal to the penetration hardness of copper would be the level of stress if the contact were plastic. This may not appear to be consistent with the results of the tungsten tests where although the stresses were much higher the σ/J

DISCUSSION OF RESULTS AND RECOMMENDATIONS

The conclusion that steam drop
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values were comparable. The results of the tungsten versus tungsten tests show the critical maximum apparent stress to be less than 17.4 kg/mm^2 (σ/J = .455 x 10^{-3}).

It is suggested that the actual contact stress in the tungsten case is larger than the apparent hertzian stress which is calculated assuming contact between perfectly smooth and circular cylinders. This is consistent with Reference 10 wherein it is estimated that the actual maximum stress is on the order of five times the apparent one.

It is evident from equations 6.4, 6.5 and 6.7 of Reference 10 that stress affects the stability of an adsorbed monolayer in both dimensional and dimensionless form. This can be shown as follows:

These equations involve combinations of $B_2B_3x^2$ and B_2x^2 multiplied by other variables, where

$$B_2 = \frac{2\pi b^3 J}{kT_o} = AJ$$

$$B_3 = \frac{\delta_o J}{4bE_a} + 1 = BJ + 1$$

b, δ_o and E_a are properties of the adsorbed molecules

k is Boltzman's constant

T_o is a reference temperature

x = dimensionless stress = σ/J (σ/J previously defined)

Therefore for a given lubricant

$$B_2B_3x^2 = AJ(BJ+1)\sigma^2/J^2$$

$$= AB\sigma^2+A\sigma(\sigma/J)$$

and

$$B_2x^2 = AJ(\sigma^2/J^2)$$

$$= A\sigma(\sigma/J)$$

Thus the dimensional and dimensionless stress contribute to the onset of instability and therefore direct comparison of tungsten results and copper and tin results at the same dimensionless stress is invalid.

The theory [10] was derived assuming an elastic contact in supplying the strain energy. Though the tin is deforming plastically, there is still elastic deformation upon loading and elastic recovery is possible after an admolecule desorbs. Therefore, there should be no basic difference for plastic or elastic contact.

A significant discrepancy between the actual test method and the theory involves the use of finite speed in the test device. The theory is developed for an equilibrium process which allows only infinitesimal speeds. A sinusoidal frequency of 1 hertz was imposed over a sliding distance of approximately .005 inches which corresponds to a peak sinusoidal velocity of about .04 cm/sec. This could induce rate effects which would ultimately have to be eliminated from the test device or the theory altered to accommodate

for these effects.

Attempts were made to operate the apparatus at lower frequencies (.01 and .1 hertz) but no motion was visible or any change measured in voltage at the vibrator over a long period of time and it is suggested that the amplifier and oscillator are incompatible for these lower frequencies.

No quantitative measurement of the amount of tin transfer was attempted. Even when there was no obvious transfer to the smooth OFHC copper specimen there remains the possibility of a thin film. It is believed that the transfer observed to the ordinary copper specimen is due to the roughness of the specimen such that the copper plows through the tin even though with no motion a monolayer of adsorbed methanol separates the surfaces. Examination under an electron microscope of a copper specimen subjected to this type of test that has undergone no apparent transfer would give more information on this film.

Along with lower speed, improvement is also desired in the range of stress and the confidence with which the stress is actually known. With specimens undergoing plastic contact (that is, not only the softer materials but also harder materials with rough surfaces) the stress is known with a high degree of confidence but in general cannot be varied without changing the materials. Surfaces smooth enough for elastic contact are very difficult to obtain and

considerable effort has gone into the development of the preparation technique for the tungsten specimens used. The stress is dependent on the cube root of the normal load and inversely proportional to the two-thirds power of the specimen diameter for equal diameters [13]. Thus wide changes in load are required to achieve substantial changes in stress. A larger diameter specimen would serve to reduce the stress, which is desired to extend the tungsten results, but an increase in the surface roughness and departure from known circularity at the area of contact are then to be expected. Reduction in load with the tungsten specimens is perhaps feasible but at low loads stray vibration and system sensitivity become a problem, particularly when using resistance measurements as an indication of surface separation.

It would be advantageous to develop a system capable of stress variation from approximately 6 to 60 kg/mm^2 to evaluate the critical stress for methanol. When such a system is built, other parameters such as temperature, vapor pressure and lubricant can be easily varied. The most promising method of operating at a known low stress level appears to be by using different materials of low hardness. This has the disadvantage of changing many other material properties along with the level of stress.

Resistance measurements were not found to be very useful. The data showed an increase in resistance when lubrication

was eliminated on purpose. The resistance also became more erratic, which is thought to be due to formation of debris or wear fragments. This was the opposite effect to that anticipated, as a lower resistance was expected when the methanol desorbed. This increase would not be as significant in an actual contact undergoing a change in stress in an atmosphere of methanol, as the stress would vary slowly over the area of contact and no sudden uniform change in stress over all the contact area would occur. This is demonstrated in the results at high load with the tungsten specimens where the resistance decreases with increased load as would be expected.

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APPENDIX A

APPLICATION TO NAVAL ENGINEERING

The specific problem or the results are not directly applicable to naval engineering. In the long term, however, if this thesis and other research contributes to the clear understanding of boundary lubrication, the Navy and indeed all users of lubricated equipment will undoubtedly benefit.

It is also hoped in the shorter term that the experience in the general area of lubrication the author of this thesis has obtained will enable him to contribute to the better engineering of naval and other ships.

APPENDIX B

THE APPARATUS

It was intended that the test device have the following features:

a) a specimen holder that could be transferred to the optical microscope for visual examination with a high probability of finding the area of contact

b) specimen holders with two point support for the specimens allowing contact in a region of controlled atmosphere, allowing reciprocating motion of small magnitude and allowing electrical contact on both ends of the specimen.

c) ability to load the contact to as low load as possible, while still providing two degrees of restraint, i.e., preventing other than vertical movement by the lower specimen.

d) ability to provide reciprocating motion to the test specimens which were crossed at 45° relative to the line of motion

e) measurement of contact resistance

f) atmosphere control such that the contact area could be exposed to a selected gaseous atmosphere containing some lubricant vapor.

The results of these intentions are shown in Figure B.1, B.2 and B.3.

The test specimens are fastened in holders (Figure B.2

FIGURE B.1

Apparatus

FIGURE B.2

Specimen holders

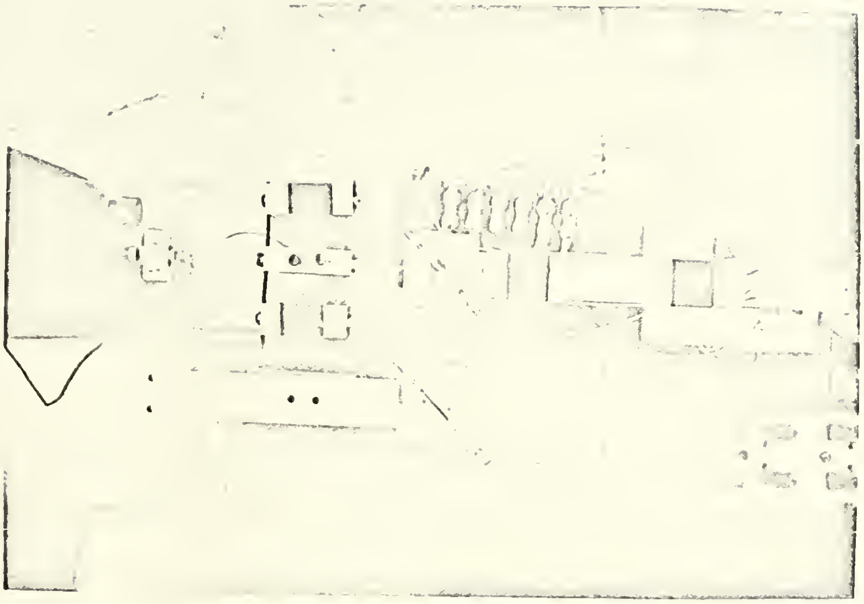

FIGURE B.3

Specimen holders, top view showing detached upper holder with OFHC copper specimen.

and B.3) and connected to the resistance measuring circuit described below. One specimen holder is oscillated while the other is loaded in cantilever fashion so that the contact area receives a normal load.

The upper specimen holder is easily detached from the oscillating drive mechanism so that the specimen could be viewed at up to 600X and photographed in a Unitron microscope. A reference point for visually finding the probable area of contact was found to be a portion of the gas supply pipe.

Clearances of about 5 thousandths of an inch as the holders are fitted over one another insure outward flow of the atmosphere supplied and assist in positioning the specimens so that the probable area of contact can be located prior to running and this same area examined after testing.

Oscillating motion power was supplied by the following equipment:

Oscillator Krohn-Hite, Cambridge, Mass., Model 440A, .001 hz to 100 khz., sine wave output with voltage control was utilized

Amplifier MacIntosh 40 Monaural Audio Amplifier

Vibrator 3 ohms Goodman's Vibrators Ltd. vibrator manufactured by Pye-Ling Ltd., Royston-Herts England

A separate one amp fuse protected the vibrator from excess amplifier output.

Small 60 hertz noise in the oscillation was discernable at very low frequency (.001 to .1 hz), however, the results were primarily taken at 1 hz and therefore no attempts were made to reduce or eliminate the hum.

The atmosphere was supplied by bottled pre-purified nitrogen gas which was saturated with lubricant vapor by bubbling through a fritted glass tube immersed in liquid lubricant. The gas was checked for saturation by slightly cooling the flow and insuring that condensation occurred.

Measurements of resistance were made by a Sanborn 150 recorder using a Low Level Preamplifier set to a sensitivity of 100 microvolts per centimeter of deflection. Resistance measurements from thousands to thousandths of ohms were recorded. The circuit supplied a current through one end of each specimen and measured the voltage across the other end of both specimens. It was similar to that pictured by Holm in Figure 8.03 of [14]. Current was supplied from a 1.5 volt dry-cell and was controlled by resistors in the supply circuit from current values of about 5 microamperes to 16 milliamperes.

APPENDIX C

THE SPECIMENS: THEIR PREPARATION AND POLISHING

The tungsten specimens were prepared from hard-drawn, ground (sealing-grade) tungsten wire .060 inches in diameter. The minimum tungsten content is 99.95 per cent. The surface is mechanically polished with 3/0 metallographic paper in a drill press, rinsed in hot tap water followed by distilled water and then electropolished.

The polishing solution consists of 25% .2 molar sodium hydroxide (NaOH) and 75% .4 molar sodium tartrate ($Na_2C_4H_4O_6.2H_2O$). The specimens are immersed in the solution while being rotated in a drill press and the beaker of solution is rotated also. Approximately 6 volts is impressed and a current of about 150 milliamperes flows through the circuit for a current density of about 10 amps/decimeter^2. After polishing for 15 minutes the specimens are rinsed with distilled water and methanol. The surfaces were examined at 300X in an optical microscope, and generally appeared very smooth except for occasional pits, probably due to inclusions or impurities, small compared to both the predicted and observed contact area. The upper specimen was examined after placement in its holder with particular attention paid to the anticipated area of contact. Specimens prepared in the same manner are shown in Figure 2.2 of [10] and are further discussed in [15].

The tin coated specimens were made by coating a copper wire with reagent grade, ACS, tin from a bar using a standard soldering iron. The surface was cleaned with methanol to remove the soldering flux. Fresh metal was exposed with a razor blade and then rolled with a glass rod to smooth the surface.

The copper specimens were electrolytically polished in a 0.9 molar solution of orthophosphoric acid at 1.5 volts with a current density of about 3.5 amps/decimeter^2. [17] The specimen was immersed horizontally in the solution about $1\frac{1}{2}$ inches below a copper plate which served as the cathode. The upper surface polished well and was used for the contact zone. The lower surface appeared to have the stryations from the 3/0 mechanical polishing preparation emphasized.

APPENDIX D

SUPPLEMENTARY RESULTS

This section will present in greater detail the data measured and observed from which the previous results were derived.

A. TUNGSTEN ON TUNGSTEN

Many measurements were made of contact resistance between the two tungsten specimens. Samples of these measurements are presented in Tables D.1 through D.3. As can be seen in these tables, resistance values ranged from a high value of 5,000 ohms to a low of .37 ohms at the same load (1/3 gram). The results were not repeatable, except in general, at higher loads (greater than about 1 gram) where the resistances measured were within a factor of three from highest to lowest value. At best, the low resistance values serve to imply the lack of a complete monolayer of adsorbed lubricant between the specimens.

It was observed that at loads of one gram and above, when supplied with methanol vapor, the indication of voltage as measured on the Sanborn recorder was steady following the relative motion of the contacts imposed by vibration. Voltage indication in the nitrogen atmosphere was erratic both during and after motion and an estimated average value is presented in Table D.2. Under visual observation at 300X the specimen surfaces appeared obviously

APPENDIX B

SUPPLEMENTARY RESULTS

This section will present in
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A. TUNGSTEN ON TUNGSTEN

Many measurements were
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scratched and so it is proposed that unsteadiness of the resistance measurement is due to the build up of wear particles coupled with slight movement of the apparatus due to vibration induced by machinery in the area. It is also proposed that these stray vibrations are the source of unsteady measurements with methanol vapor at low loads.

These inadvertent vibrations were greatly reduced by mounting the actual test device on a heavy bedplate and in turn mounting this plate on soft pads. However, the circuit was still very sensitive and dropping a 2 gram weight on the heavy bedplate could be noticed in voltage measurement at the very low loads (1/6 gram).

Visual observations of the specimens after vibration which are described in Table D.3 provided another indication of lack of a complete monolayer of adsorbed lubricant between the tungsten specimens. The discolored area appeared as a light brown film, slightly darker at the ends of the major axis of an elliptically shaped apparent contact zone. The other recurring type of contact zone appearance was similar to pits observed on the tungsten surface in areas where polishing was not fully effective. These spots could be actual surface damage or perhaps could be due to condensation of lubricant in the contact area. The spots were not removed by blowing dry air or nitrogen on the area; and wiping lightly with lens tissue affected the surface finish to such

an extent that conclusions concerning the appearance of the contact zone after wiping were not possible. The contact zone after vibration at higher loads appeared similarly pitted to a larger extent and thus the pitted appearance seems to indicate surface damage.

The higher resistance values shown in Table D.3 did correlate with what appeared to be lesser surface damage but no quantitative conclusions could be drawn.

The contact zones in the methanol atmosphere, however, even at loads up to 15 grams were not damaged in the same manner as when only nitrogen was supplied. The discoloration and apparent pitting with methanol vapor were very distinct from the scratches which were visible over the contact area in the nitrogen atmosphere.

These visual observations, in addition to the characteristics of the voltage measurements in each atmosphere described above, form the basis for the conclusion that the atmosphere containing the methanol vapor provides some lubrication although there does not appear to be a complete insulating monolayer formed.

Thus there was no basis for forming a quantitative conclusion concerning the effect of stress on this type of lubrication.

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contact zone after wiping were not possibl
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Thus
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TABLE D.1

RESISTANCE DATA FOR TUNGSTEN ON TUNGSTEN NITROGEN SATURATED WITH METHANOL AT ROOM TEMPERATURE

Date: April 22, 1970

Load (grams)	1/3	2/3	1.0	1/3	2/3
σ(kg/mm^2)	23.0	29.0	33.2	23.0	29.0
$\sigma/J \times 10^3$	.603	.759	.872	.603	.759
Resistance	105.	.37	.54	5.0	.60
(ohms)	5000.	.6	.26	.4	.16
"	27.8	.4	.26	1.2	.32
"	.925	.32	.82	1.6	.15
"	.37	.38	.3	.6	.4
"	26.0	1.2		.3	.24
"	2.22	.76		.58	.32
"	.55	.2		.6	
"	.463				
"	1.76				

TABLE D.1 (continued)

Date: April 24, 1970

Load (grams)	1/3	2/3	1.0	1/3	2/3
$\sigma(kg/mm^2)$	23.4	29.5	34.0	23.4	29.5
$\sigma/J \times 10^3$	.615	.774	.890	.615	.774
Resistance (ohms)	.6	2.1	.2	1.25	.56
	1.4	2.3	.21	.7	.6
"	8.2	1.28	.2	1.25	.34
"	5.4	.72	.3		
"	33.0	.56	.8		
"	20.0	.44	.7		
"	10.0	.32			
"	15.0	.46			
"	10.8				

TABLE D.1 (continued)

Date: April 25, 1970

Load (grams)	2/3	1.0	1 1/3	1 2/3	2	3	4
$\sigma(kg/mm^2)$	29.5	34.0	37.4	40.3	42.8	49.0	54.0
$\sigma/J \times 10^3$	.774	.890	.98	1.055	1.12	1.286	1.41
Resistance	2.5	2.0	1.16	.15	.28	.265	.18
(ohms)	12.8	6.0	3.0	.27	.27	.36	.11
"	5.0	8.2	8.3	.21	.17	.115	.23
"			2.2				

Load (grams)	5	6	7	8	9	10	12
$\sigma(kg/mm^2)$	58.0	62.0	65.0	68.0	70.6	73.0	78.0
$\sigma/J \times 10^3$	1.52	1.62	1.70	1.78	1.85	1.91	2.04
Resistance	.062	.07	.055	.0425	.05	.074	.068
(ohms)	.102	.105	.045	.0525	.043	.055	.068
"	.185	.06	.05	.053	.05	.05	.05
"	.175			.036			

NOTES

Note 1. Resistance obtained by measuring voltage across contact with known current flowing through contact. Specimens vibrated at 100 hz. for approximately 1 minute prior to voltage reading. Measurements are sequential.

TABLE D.1 (continued)

Note 2. σ max. = maximum apparent hertzian stress for elastic contact between cylinders.

$J = E/(1-\nu^2)$

E = Young's modulus

ν = Poisson's ratio

Note 3. Each date's results were taken from a single contact zone; that is, no definite change of anticipated contact area was made.

TABLE D.2

RESISTANCE DATA FOR TUNGSTEN ON TUNGSTEN IN NITROGEN ATMOSPHERE AT ROOM TEMPERATURE

Load (grams)	1/3	2/3	1.0
$\sigma(kg/mm^2)$	23.4	29.5	34.0
$\sigma/J \times 10^3$	.615	.774	.890
Resistance (ohms)	2.5	9.2	450
	off scale	70	40
"	9.0	78	27
"	100		

Note 1. Data obtained April 24, 1970.

2. Surfaces of both specimens had scratches in area of anticipated contact zone.

3. Resistances were measured after vibration of contacting specimens for approximately 30 seconds at 100 hz.

TABLE D.3

RESISTANCE AND VISUAL RESULTS FOR TUNGSTEN ON TUNGSTEN IN NITROGEN SATURATED WITH METHANOL VAPOR

Run	Resistance (ohms)	Visual appearance of expected contact zone
1	5.8	no contact zone apparent
2	5.0	slight discoloration (light brown)
3	2.0	brown colored area
4	1.6	dark spots that appear like pits in the metal
5	.8	brown edge
6	2.5	area with pitted appearance
7	1.6	brown colored area

Note 1. Data at 1/6 grams ($\sigma/J = .455 \times 10^{-3}$) $\sigma = 17.4$ kg/mm^2
σ = maximum apparent hertzian stress

2. Run consisted of:
   a) inspecting probable area of contact using center of upper specimen holder as a reference
   b) loading to desired load
   c) allowing about 2-3 minutes to settle
   d) imposing relative motion at 1 hz. for 2 minutes
   e) measuring resistance when settled
   f) visual inspection at 150 & 300X
   g) each test was run on a new contact area

3. All areas approximately identical size

4. Data obtained on May 4, 1970

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